

LABORATORY SPECTRA OF C₆₀ AND RELATED MOLECULAR STRUCTURES

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The electronic spectra of fullerene structures in high frequency discharge are studied in the plasma chemistry laboratory of the Faculty of Science of Masaryk University in Brno. The ultraviolet and visual spectra are investigated in order to be compared with the diffuse interstellar bands and interpreted within the theory of quantum mechanics. The preliminary results of the study are presented here in the form of a poster.

It is more than two centuries since the Swiss geometrician Leonhard Euler proved the existence of closed spheroidal surfaces composed of twelve pentagonal and a variable number of hexagonal planar faces. In the past decade, the structures occupied by carbon atoms and ions engrossed theorists in the molecular dynamics, and the mathematical theory of Euler began to be used for theoretical modelling of special, highly stable molecular clusters termed fullerenes. It was found that there exist at least one or two configurations of carbon atoms predisposed to form soccer-ball-like molecules characterized by a high degree of symmetries, namely C₆₀ and C₇₀.

The fullerenes and other related structures soon became a centre of interest of astrophysicists who explained some specific properties of absorbing matter in the interstellar space with the presence of these strange, large molecules. Even though contradictory facts still exist, it seems compelling enough to accept that the absorption peak at 217 nm, which has long been attributed to small particules of graphite (Huffman, 1977), might be produced by the giant spheroidal molecules composed of sixty atoms of carbon and structured in a pentagonal and hexagonal polyhedral net, characteristic of the very fullerenes (Krätschmer et al., 1990).

Because polyhedral carbon clusters appear to be excellent candidates for carriers of diffuse interstellar band opacities observed in the circumstellar environment (Léger et al., 1988), a laboratory determination of their ultraviolet and visual absorptions would be most useful. In spite of grave experimental difficulties, very sophisticated techniques have been developed that now enable the synthesis of fullerenes

in macroscopic quantities by vaporizing graphit under specific thermodynamic conditions. Thus, polyhedral carbon molecules can now be produced by laser irradiation or with resistive heating of graphit and they can be formed in a sooting flame or in an electric arc. It was discovered that various stable fullerenes could be synthesized in this way (with 32 and even more carbon atoms arranged at the same number of vertices of truncated icosahedrons) but only C_{60} and C_{70} can be prepared in quantities enabling an investigation of their physical properties. This paper describes two experiments designed to produce fullerene molecules in the laboratory as well as to study the processes of their formation.

The first experiment was fulfilled in the arrangement used many times for producing superconductive films by the deposition technique. In contrast to the common low pressure chemical vapour deposition, our radio frequency deposition of C_{60} works at atmospheric pressure, and, without requiring a high vacuum, permits a wide variety of processing environments. The carbon films containing fullerene molecules were produced by thermal vapour depositions in a radio frequency unipolar plasma.

Using the radiofrequency of 27 MHz, carbon films, rich on fullerenes, were produced on a mono-crystalline silicon substratum by the technique of depositions on the plasmatically vaporized chemical aerosols. The ions contained in the aerosol mist were generated in an ultrasonic nebuliser and were injected through an electrode into the plasma region. The high frequency generator of the power output of 1.5 kW working at 27 MHz was connected through a matching network with a graphite electrode. The toluene diluted by argon was used as the carrier gas. Once the liquid precursors were evaporated into the plasma, they decomposed and reacted in the boundary layer over the substrate to form a fullerene abundant carbon film.

As the extensive heat flux from the plasma plume to the substratum rose during the deposition processes, the substratum immersed in the upper part of the unipolar high-frequency plasma had to be thermally connected with a special air cooled holder. Such effective cooling of the substratum is crucial for controlling the microstructure of the film and to minimize the film-substratum interactions. It is worth noting that the substrate temperature could also be controlled by a special arrangement in the flow of the carrier gas.

Different substrate temperatures in the range of 200 up to 10000°C were used to deposite the fullerene rich film of carbon onto the substratum. Depending on the concentration of the toluene in the carrier gas flow and on the position of the substratum in the high-frequency plasma, the deposition rate was between 300-120 nm/min, and the film thickness varied between 0.4 - 2 μm .

The deposited samples of fullerenes were treated for laboratory measurements in the way normally used in chemical practice. They were extracted from the substratum target in redestilled, hot CHCl_3 , then the solution was evaporated in a vacuum and the residue solid extract was dried and finally dissolved in n-hexane. The UV absorption spectra of the resulting solution were measured in a quartz cell. Contamination by "UV impurities" made it very difficult to evaluate these spectra, because

of the peak of C_{60} at 213 nm that might be blended by the band corresponding to trichlormethane that was not completely removed. For this reason, the reference solution was prepared in the same manner so that the corresponding absorption curves could be compared to each other. From the smooth course of the reference curve, it could be deduced that the peak at 252 nm had been produced with a new constituent in the solution. Later, after evaporating the hexane, the solution could be seen in a crystallic form through a microscope as expressing all the features of a genuine fullerite. The original record of the absorption curve of the fullerite is given in Figure 2. It can be compared with the absorption curve of the pure C_{60} in Figure 3.

This experiment has shown that besides many sophisticated ways developed to synthesize fullerenes for practical use, there may still exist other techniques suitable for producing them in macroscopic quantities. From this point of view, the results may be of interest to those who are engaged in the technological aspects of forming these large molecules in an artificial way. But there are other aspects that may give a new importance to this technique, especially regarding the possibility of understanding better and explaining the processes that lead to the formation of fullerenes. This very aspect is important for astrophysicists because, to a certain extent, it can contribute to interpretations of the carriers of the diffuse interstellar bands. From the astrophysical point of view, the experiment surely might attract the interest of those who are engaged in solving the problems of the formation of fullerene molecular structures in a close stellar environment or even in the interstellar space. Except for the high frequency electromagnetic field, one can suppose that the conditions for the formation of fullerene molecules in our experiment should be similar to those prevalent in atmospheres of some types of highly evolved stars producing a carbon constituent of the interstellar matter (e.g. of carbon stars). That is why we decided to rearrange and to repeat the experiment once again and direct it this time at the spectroscopical investigation of problems connected with the formation of fullerene structures in plasmatic environments.

The arrangement of the new experiment is similar to that already realized, only the cylinder demarcating the space of the plasmatic discharge has been replaced with one of quartz. For the spectrometric measurements, the apparatus was completed with a Seya-Namioka monochromator with concave diffraction grating enabling the study of spectral features of the discharge in the range of 200 to 600 nm. Using an accessory source of high temperature continuum light, one also has the possibility of getting the absorption spectra of carbon molecular clusters. The experiment is schematically described in Fig.1 and is now at a stage of testing. The first results enabling a theoretical interpretation of the formation of large molecular clusters of carbon from their less complex fragments are expected to be obtained in the second half of the year.

First note added in proof:

When discussing the fullerene structures as possible carriers of the DIBs, one should take into account that the spherical fullerenes are not the only possible isomers of the polyatomic carbon type molecules. It seems a puzzle to regroup the carbon pentagons and hexagons in fullerene cages into another configurations but the fact is that, in this manner, we can get tubules at both sides closed by two covers each composed of six pentagons and unlimited number of hexagons. In Fig.4, which graphically describes the rod-like cage carbon structures $C_{(n,12)}$ ($n = 2,3,4,\dots$), the graphitic tubule lattices arise by wrapping the honeycomb lattice on a cylinder whereas each cover is formed from a hexagon surrounded by six pentagons. One can object that the stability of the covers must not be too high (Kroto 1987) but the free bounds at the ends of the tubules can be occupied with hydrogen atoms and a special type of polyatomic hydrocarbon tubules formed. It is beyond question that this kind of hypothetical molecular structures should express specific polarizing features in the interstellar space. Does anybody succeed in trying to compute their stability and their electronic rotation-vibration spectra?

Second note added in proof:

Only little changes are needed to rearrange the experiment in order to form fragments of fullerene-like cage structures based on silicon. It is worth noting at this place that silicon clusters are currently of growing interest as new materials with interesting properties (Kobayashi, Nagase, 1993) and that the cosmical abundance of silicon is comparable with those of carbon. Thus, even though there is a strong chemical bond between silicon and oxygen in astrophysical environments, some atoms of silicon may form fullerene-like structures. Why not to take them into consideration also in investigating the carriers of DIBs?

Third note added in proof:

Even if there is no evidence that fullerenes are present in cometary atmospheres which are otherwise rich on the carbon compounds, one can think about the way how to detect them by IR spectroscopic measurements. It is known that the light from stars is affected only a little when passing through a dilute cometary coma. However, in case of "occultation" of an early type star by the innermost region of coma, some absorption features of cometary origin could be seen in the spectrum.

An extensive list of comets is being prepared for selection of target objects to be observed by the Infrared Satellite Observatory (launch scheduled on Autumn 1995). During next 18 months (the assumed active lifetime of the satellite) comets P/Kopff, P/Churyumov-Gerasimenko, P/Wild 2, and also P/Schwassman-Wachmann 1 and 3, P/Encke, P/d'Arrest, P/Honda-Mrkos-Pajdusakova are expected to be bright

and observable. Spectrophotometry in the region of 2-12 microns by ISO/ISOPHOT instrument and simultaneous Earth-based visible spectroscopy and photometry of comets will include also the observations of selected stars "occulted" by comets. Unfortunately, due to various perturbations in the motion of comets and due to the hardly predictable cometary activity in developing atmospheres no definitive selection of stars with suitable spectra can be made. The candidate stars, located in the about 10' wide strip on sky along the predicted path for every of the target comets, are surprisingly few, only 2 to 10 for each target comet. So it will deserve a cooperation between observatories to fulfill this program.

Thus, even if there is no evidence that fullerenes are present in cometary atmospheres, one may hope that these proposed observations could bring at least upper limits for the concentration of DIB's carriers of any kind in comets.

References:

- Ajie, H., Alvarez, M.M., Anz, S.J., Beck, R.D., Dietrich, F., Fostiropoulos, K., Huffman, D.R., Krätschmer, W., Rubin, Z., Schiver, K.E., Sensharma, D. and Whetten, R.L.: 1990, *Jour. Phys. Chem.* 94, 8630
Huffman, D.R.: 1977, *Adv. Phys.* 26, 129
Krätschmer, W., Lamb, L.D., Fostiropoulos, K. and Huffman, D.R.: 1990, *Nature* 347, 354
Kroto, H.W.: 1987, *Nature* 329, 529
Kobayashi, K. and Nagase, S.: 1993, *Bull. Chem. Soc. Jpn.* 66, 3334
Léger, A., d'Hendecourt, L., Verstraete, L. and Schmidt, W.: 1988, *Astron. & Astrophys.* 203, 145.